Probing the dielectric constant at the nanoscale: from thin films to DNA and confined water

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The dielectric constant (or electric polarizability), ϵ_r , is a fundamental physical property of matter which depends on chemical composition, structure and phase. It plays a crucial role in a wide range of phenomena and disciplines, from physics and materials science to chemistry and molecular biology. For example, in physics, it is inherently linked to charge storage and electric transport. In biology, it modulates long-range electrostatic and van der Waals interactions that are crucial for macromolecular assembly and interactions. Yet, probing local dielectric properties has remained a long-standing technical challenge because the signals that have to be detected are extremely weak and buried into non-local and geometric artefacts.

In the first part of my talk, I will review our work in which we showed that the dielectric constants of nanostructures and biological molecules can be measured at low frequencies (< 1 MHz) with a scanning probe using both the current-sensing [1,2] and electrostatic force-sensing [3,4] approach. We determined the dielectric constants of a variety of nanostructures and biological samples for the first time: from thin oxides and biological membranes [1,2,6] to single nanoparticles [3], viruses [3,4] and bacteria [5]. Importantly, we resolved the dielectric constant of DNA in a native condensed state [4], which had remained unknown. We found it ~ 8 , sensibly higher than commonly assumed in theoretical calculations, and showed that it is a critical parameter for a realistic computational description of DNA-DNA and DNA-protein interactions. Furthermore, we showed that local dielectric measurements can be done in electrolytic environment [7], which is of great importance for electrochemical and biological applications, and extended up to the microwave regime (GHz frequencies) [8].

In the second part of my talk, I will present our latest results in which we were able to measure the dielectric constant of few water layers confined between two atomically thin crystals [9]. For many decades, it has been speculated that the dielectric constant of water near surfaces should be different from that of bulk water. This has major implications because water's dielectric constant directly affects various forces between microobjects and macromolecules. In turn, these forces define many fundamental phenomena in nature such as hydration, ion solvation, chemical reactions and macromolecular assembly, to name but a few. Despite a massive amount of literature and of atomistic simulations, the absolute value of the dielectric constant of near-surface water and how far its anomalous behavior (if any) extends into the bulk had remained unclear so far. Our experiments revealed the presence of an interfacial layer with vanishingly small polarization such that its out-of-plane ϵ_r is only ~ 2 . The electrically dead layer is found to be two to three molecules thick, in agreement with the thickness predicted by molecular dynamics calculations. Our results provide much needed feedback for theories describing water-mediated surface interactions and behaviour of interfacial water, and show a way to investigate the dielectric properties of other fluids and solids under extreme confinement.

References

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